VI. *The Ultra-Violet Band of Ammonia, and its Occurrence in the Solar Spectrum.*

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[Plate 2.]

Introductory.

A question of great interest in connection with the solar spectrum is that of the origin of the thousands of unidentified faint lines which were catalogued by Rowland in his "Preliminary Table of Solar Spectrum Wave-lengths." Some of these lines may possibly be identical with faint lines in metallic spectra which have not yet been completely tabulated, but in view of the presence of bands of cyanogen, carbon and hydrocarbon, the possibility of the correspondence of most of them with band spectra of other substances should not be overlooked.

As a contribution to this inquiry, the present investigation was undertaken primarily in order to determine whether Group P in the ultra-violet region of the solar spectrum might not be mainly due to the presence of ammonia in the absorbing atmosphere of the sun. Ammonia was already known to give a remarkable band in this region, having its position of maximum intensity near λ 3360, but it had not been investigated in sufficient detail to permit of an adequate comparison with the solar tables. Photographs have accordingly been taken with spectrographs of high resolving power for the purpose of this comparison, and, as will appear from the details which follow, it has been established that the ammonia band is certainly represented in the solar spectrum, and accounts for a considerable number of faint lines for which no other origins have been suggested.

In view of the unusual appearance of the band, an attempt has also been made to elucidate the chief features of its structure.

Previous Observations.

The characteristic ultra-violet band of ammonia, about λ 3360, appears to have been first described by Eder, who observed it in the flame of ammonia burning in

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oxygen.* Other bands in the ultra-violet which were attributed to ammonia by EDER were afterwards found to be identical with DESLANDRES' third positive group of bands of nitrogen. New determinations of the positions of the ammonia bands in the visible spectrum were also made by EDER, but it is not necessary to consider these for the present investigation. In the case of the ultra-violet band, the thirty-four wave-lengths tabulated by EDER evidently refer to unresolved groups of band lines, and only serve for identification when instruments of small resolving power are employed.

More recently, the band has been described and illustrated by LEWIS, as it appears in the spectra of vacuum tubes containing mixtures of nitrogen and hydrogen.† Its occurrence was observed with these gases in any proportion, but not in the case of either gas alone. As obtained in this way, the band was complicated by superposed bands of nitrogen, and higher resolution than that employed was considered necessary to effect the separation satisfactorily.

The band in question has been noted occasionally in various experiments carried on at the Imperial College during several years. It has been observed in the flame of imperfectly dried cyanogen, in the spectra of vacuum tubes, and with enclosed arcs under reduced pressure, as well as in the ammonia flame itself. In all cases the band appeared under circumstances in which its presence could be attributed to combined nitrogen and hydrogen, but the spectroscopic evidence does not exclude the possibility of some combination other than ammonia. In the course of the present investigation it has further been found that the brighter parts of the band sometimes occur feebly in the spectrum of the copper arc, and even in that of the ordinary carbon arc in air.

Experimental Procedure.

A preliminary investigation was undertaken to find a source that would give the band sufficiently isolated, and at the same time bright enough to be photographed with high dispersion. Vacuum tube methods proved unsatisfactory on account of the superposition of bands of nitrogen. The purest band was obtained from an ammonia flame fed with oxygen. An ordinary blowpipe was found to be a convenient arrangement, ammonia being passed through the outer tube, and a stream of oxygen through the inner one. The apparatus employed is illustrated in fig. 1. Ammonia of specific gravity 0·880 contained in the flask A was heated by a Bunsen flame, but not sufficiently to cause the liquid to boil. The vessel B was introduced as a means of condensing most of the water vapour, which otherwise condensed in the tubes of the blowpipe and extinguished the flame. The mercury gauge at C provided a convenient means of measuring the pressure, which was maintained at about 10 cm. of mercury. Oxygen was supplied from a cylinder of the compressed gas. The

* 'Denkschr. Wien Akad.,' vol. 60, p. 1 (1893).

† 'Astrophys. Jour.,' vol. 40, p. 154 (1914).

flame produced in this way could be kept fairly steady, and had a small, but intensely bright, central core of a yellow colour, which was surrounded by a paler envelope. The flame was pointed in the direction of the collimator of the spectrograph, and an image of the bright central core was focussed on the slit by a quartz lens. Photographs were first taken with a small quartz spectrograph giving a dispersion of about 60A per millimetre at λ 3360, and with a quartz Littrow instrument giving a dispersion in the same region of 7A per millimetre.

In view of the need for the highest attainable resolution of the central parts of the band, an attempt was made to photograph the spectrum of the flame in the 3rd order of a 10-foot concave grating, in which the dispersion is 1·85A per millimetre. An exposure of 12 hours, however, yielded only a feeble trace of the band, and it was

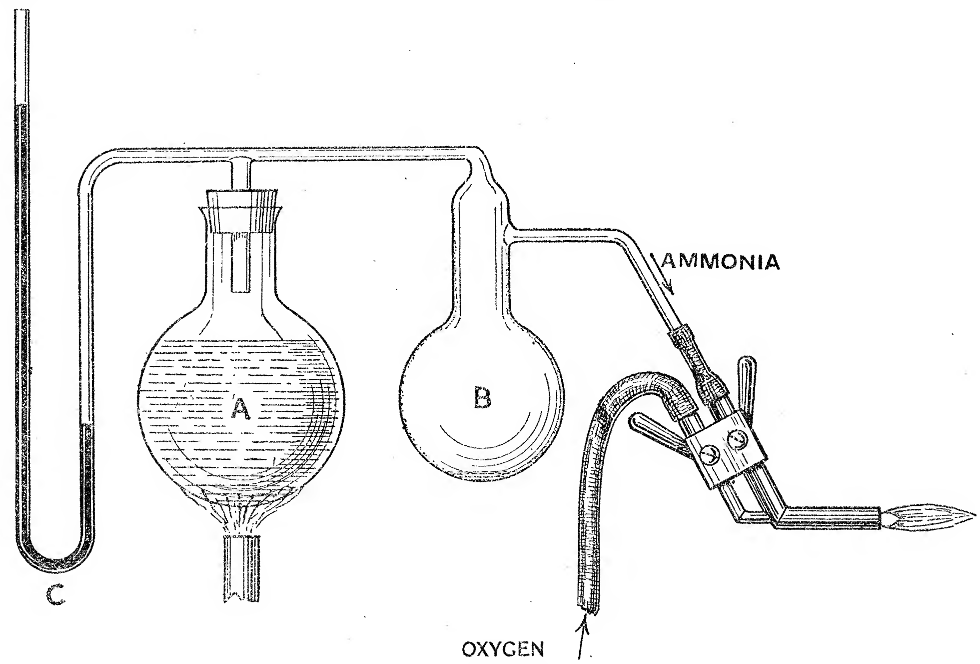


Fig. 1. Apparatus employed for ammonia flame.

evident that very much longer exposures would be necessary to give satisfactory photographs for measurement. Difficulties were anticipated in maintaining steady instrumental conditions, as the regular mounting is still detained in Russia, and only a temporary arrangement of the grating was available.

Advantage was therefore taken of the possibility of producing the band in the electric arc, which had previously been noted in the course of experiments made for other purposes. In the first arrangement tried the arc was enclosed in a glass globe provided with side tubes for the admission of the electrodes, and with a quartz window through which the arc could be observed, as in a previous investigation on the spectrum of magnesium.* It was found, however, that the quartz window became obscured by the condensation of water-vapour, and it was therefore replaced

* 'Phil. Trans.,' A, vol. 209, p. 449 (1909).

by a metal disc having a small aperture through which the light of the arc could pass to the spectrograph. A constant stream of ammonia, which was drawn off by a water pump, was caused to flow through the apparatus. The arc was on a 200-volt circuit, and the current used was 1·8 amperes. The electrodes were of copper.

The grating was mounted so as to give a normal spectrum, and precautions were taken to avoid mechanical displacements. The temperature of the laboratory was also kept as constant as possible during the exposures, which were of about 60 minutes' duration. An internal shutter, detached from the other parts of the spectrograph, was arranged next the plate to allow of two comparison spectra being photographed, one before and one after the ammonia spectrum.

A photograph of the copper arc in air, which was taken to facilitate the elimination of lines introduced by the electrodes, showed that the copper employed contained impurities of nickel and silver. In the case of very strong lines, "ghosts" were also present, and there were a few lines belonging to the second and fourth order spectra; these are marked by double dots in fig. V., Plate 2.

The ammonia band occurs incidentally in an excellent photograph of the magnesium arc under reduced pressure, taken in 1913 by Mr. W. JEVONS, in the 4th order of the 10-foot grating; the band is here somewhat confused by nitrogen, but many of the ammonia lines can be quite certainly identified, and the high resolution has been of special value in connection with very close groups near the extreme ends of the band.

General Description of the Band.

The general features of the ammonia band will be best gathered from the photographs reproduced in Plate 2. With low dispersion, as will be seen from fig. I., the band resembles a double line having components of unequal intensity, but there are indications of banded structure on both sides in photographs which have received sufficient exposure. With somewhat higher dispersion, as in fig. II., the real structure of the band becomes more evident; it shows a closer resemblance to the ordinary type of band, such as those found in nitrogen, with the exception that the component lines fade off in both directions from the apparent head.

In fig. III., taken with the still higher dispersion of the quartz Littrow spectrograph, many of the band lines are resolved into groups of three, which cannot properly be called triplets on account of the variable spacing. The central maximum about 3360, however, remains imperfectly resolved. With the highest resolution employed—that of the 3rd order grating—additional groups of three are separated, and the central maximum is seen to consist of a great number of closely crowded lines (figs. IV. and V.). The secondary central maximum about 3371, which corresponds to the weaker component of the doublet which represents the band with low dispersion, is also resolved into a large number of component lines. It will be observed that while the central maximum degrades in both directions, the secondary maximum degrades only towards the red.

In the arc, the central and secondary maxima are more fully developed than in the flame, in the sense that the band lines extend to greater distances from the two heads. That the majority of the additional lines are really due to ammonia, and have not been introduced from other possible sources in the arc, is sufficiently proved by the series investigation, which shows that many of them are associated with the lines which appear in the flame. This greater development of the central parts of the band in the arc is accompanied by a weakening of the groups of three in the vicinity of the maxima, and a relative intensification of those further away.

Similar modifications have also been noted in the case of vacuum tube spectra when discharges of different intensity have been employed. No special experiments have been made in this connection, but in some photographs of the spectrum of nitrogen where ammonia appears as an impurity, it has been observed that the groups of three near the central maxima are developed relatively strongly by feeble discharges, while strong discharges enhance the groups away from the maxima. Increased intensity of discharge thus appears to produce the same change of spectrum as the increase of temperature in passing from the flame to the arc.

Estimates of the intensities of the lines in both flame and arc have accordingly been included in the general list (Table V.), but the comparison of the two sources in the region of the central maximum is incomplete on account of the smaller resolution in the photographs of the flame spectrum.

The wave-lengths of the lines were determined in the usual manner by interpolation with respect to lines of iron, as given by Burns. Lines of nickel originating in the poles employed for the arc spectrum, for which wave-lengths are also given by Burns, served for the detection of small displacements of the reference spectra, and to indicate the corrections to be applied. Most of the lines could be measured on the grating plates of the arc spectrum, but some were obscured by lines due to the poles, and their positions were necessarily determined from the quartz Littrow photographs of the flame spectrum. It is hoped that in most cases the wave-lengths are accurate to within 0·01A.

Details of the wave-lengths and intensities are included in Table V.

Structure of the Band.

The Groups of Three.—A considerable amount of regularity in the structure of the ammonia band is obvious by mere inspection of the photographs. This is especially the case with regard to the groups of three, which extend for more than 70A on each side of the central maximum. There are three series on the less refrangible side which coalesce towards the red, and three on the more refrangible side which coalesce towards the violet. To facilitate discussion, those on the less refrangible side have been designated α, β, γ, and those on the more refrangible side δ, ϵ, ζ, in order of increasing refrangibility in the groups of three in each case.

Data for the consideration of the regularity in these series are collected in Tables I. and II., the first referring to α, β, γ, and the second to δ, ϵ, ζ. The wave-

TABLE I.—The Series α, β, γ.

α series.				β series.				γ series.			
λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.
3450·36	28,974·34			3450·36	28,974·34						
		28·33				28·33					
46·99	29,002·67		− 3	46·99	29,002·67		− 2				
		28·05				28·13					
43·66*	030·72		− 3	43·65*	030·80		− 3				
		27·77				27·85					
40·37*	058·49		0	40·35*	058·65		1	3440·33	29,058·82		
		27·81				27·91				28·23	
37·08*	086·30		1	37·05*	086·56		1	36·99	087·05		1
		27·95				28·03				28·30	
33·78	114·25		1	33·74	114·59		2	33·65	115·35		1
		28·00				28·25				28·43	
30·48	142·25		3	30·41	142·84		2	30·30	143·78		2
		28·32				28·40				28·66	
27·15	170·57		1	27·07	171·24		4	26·93	172·44		3
		28·45				28·80				28·97	
23·81	199·02		4	23·69	200·04		3	23·53	201·41		2
		28·86				29·12				29·20	
20·43	227·88		1	20·28	229·16		1	20·11	230·61		3
		29·00				29·17				29·52	
17·04	256·88		1	16·87	258·33		3	16·66	260·13		3
		29·13				29·49				29·84	
13·64	286·01		2	13·43	287·82		4	13·18	289·97		4
		29·37				29·89				30·22	
10·22	315·38		2	09·95	317·71		4	09·66	320·19		3
		29·60				30·28				30·47	
06·78	344·98		3	06·43	347·99		2	06·12	350·66		4
		29·92				30·44				30·88	
3403·31	374·90		3	3402·90	378·43		3	3402·54	381·54		3
		30·24				30·78				31·20	
3399·81	405·14		2	3399·34	409·21		3	3398·93	412·74		5
		30·39				31·09				31·72	
96·30	435·53		2	95·75	440·30		4	95·27	444·46		2
		30·54				31·50				31·93	
92·78	466·07		3	92·12	471·80		3	91·58	476·39		7
		30·85				31·83				32·64	
89·23	496·92		− 1	88·46	503·63		4	87·84	509·03		2
		30·76				32·25				32·87	
85·70	527·68		− 1	84·76	535·88		3	84·07	541·90		8
		30·64				32·50				33·65	
82·19	558·32		− 2	81·04	568·38		6	80·22	575·55		8
		30·44				33·09				34·43	
78·71	588·76		− 8	77·26	601·47		13	76·29	609·98		16
		29·63				34·40				35·99	
75·33	618·39		− 21	73·34 ?	635·87			72·19 ?	645·97		
		27·58									
72·19 ?	645·97										

* Unresolved; separations assumed.

TABLE II.—The Series δ, ϵ, ζ.

δ series.				ϵ series.				ζ series.			
λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.
3358·04 ?	29,970·85										
		39·19									
53·63	810·04		29	3350·85	29,834·77						
		36·31				28·79					
49·55	846·35		13	47·62	863·56		−20	3346·42	29,874·26		
		35·06				30·80				28·68	
45·62	881·41		11	44·17	894·36		−4	43·21	902·94		−13
		33·99				31·23				30·00	
41·82	915·40		7	40·68	925·59		−1	39·86	932·94		−2
		33·33				31·30				30·23	
38·10	948·73		7	37·19	956·89		1	36·49	963·17		−2
		32·59				31·18				30·39	
34·47	29,981·32		5	33·72	29,988·07		1	33·11	29,993·56		1
		32·14				31·06				30·26	
30·90	30,013·46		6	30·27	30,019·13		4	29·75	30,023·82		1
		31·57				30·68				30·15	
27·40	045·03		7	26·87	049·81		5	26·41	053·97		4
		30·91				30·20				29·77	
23·98	075·94		6	23·53	080·01		5	23·12	083·74		5
		30·34				29·72				29·26	
20·63	106·28		8	20·25	109·73		6	19·89	113·00		6
		29·58				29·13				28·67	
17·37	135·86		6	17·04	138·86		6	16·73	141·67		5
		29·00				28·55				28·20	
14·18	164·86		8	13·90	167·41		8	13·63	169·87		8
		28·16				27·79				27·43	
11·09	193·02		9	10·85	195·20		9	10·62	197·30		8
		27·29				26·93				26·65	
08·10	220·31		9	07·90	222·13		9	07·70	223·95		8
		26·42				26·07				25·89	
05·21	246·73		9	05·05	248·20		9	04·87	249·84		10
		25·55				25·18				24·91	
3302·42	272·28		12	3302·30	273·38		11	3302·15	274·75		10
		24·40				24·13				23·96	
3299·76	296·68		11	3299·67	297·51		11	3299·54	298·71		11
		23·26				23·07				22·88	
97·23	319·94		11	97·16	320·58		13	97·05	321·59		13
		22·17				21·81				21·62	
94·82	342·11		15	94·79	342·39		14	94·70	343·21		14
		20·67				20·46				20·19	
92·58*	362·78		15	92·57*	362·85		13	92·51	363·40		12
		19·17				19·19				19·01	
90·50*	381·95		13	90·49*	382·04		15	90·45	382·41		
		17·83				17·74					
88·57	399·78		18	88·57	399·78		17				
		16·00				16·00					
86·84	415·78			86·84	415·78						

* Unresolved; separations assumed.

length on the international scale (λ, I.A.), the wave number *in vacuo* (ν), and the first and second differences (d_1 and d_2) are shown for each series. The figures in the

second decimal place in ν and d_1 are entitled to but little weight, but they have been included for the more consistent determination of d_2, which is given in tenths. The observed positions of some of the unresolved $\alpha\beta$ and $\delta\epsilon$ pairs are replaced by estimated positions of the components, in order that the course of the series may be more completely traced.

When due allowance is made for irregularities in the second differences, which are very sensitive to small errors in the wave-lengths, it is clear that the series as a whole cannot be satisfactorily represented by the usual approximate formula $\nu = a+b(m+\mu)^2$. Such a formula represents a series in which the distances between successive lines (d_1) are in arithmetical progression, so that the second differences (d_2) would be constant, and not one of the series approximates closely to this condition.

The actual wave-numbers of the members of the different series could only be effectively plotted on a very large scale, but the peculiarities of the series can be shown better in some respects by curves which have d_1 for ordinates, and successive integral values of m for abscissæ, the initial value of m being chosen arbitrarily. Such curves are shown in fig. 2, and it will be seen that they depart widely from the linear form implied by the above-mentioned formula. The curves also fail to show any symmetry in the arrangement of the groups of series on the two sides of the central maximum, such as might have been expected from the general appearance of the spectrum.

Considering the series α, β, γ, it will be seen that they begin with coincident, or nearly coincident, faint lines on the red side, and that the distance from line to line at first diminishes slightly and then increases. In β and γ the subsequent increase is continuous, so far as the series can be identified, and if the later lines have been correctly assigned, no other members in the immediate neighbourhood are to be expected. In the α series, the distance d_1 passes through a maximum value, as in the case of the main series of λ 3883 cyanogen which has recently been further discussed by BIRGE.* The α curve, however, differs from the cyanogen curves in having a double curvature, and while the greatest value of d_1 occurs among the weaker lines near the end of the series in cyanogen, it occurs among the brighter members in ammonia α. The later portion of the α curve is rather steep, and the identification of the next member of the series, which is involved in the secondary central maximum, is consequently difficult; the line λ 3372·19 (ν 29645·97), however, fits fairly well on the continued curve, and if this really belongs to the series it would probably be the last member.

The series δ, ϵ, ζ, resemble the first three in commencing with faint unresolved lines, which are far removed from the central maximum, but the d_1-m curves show no change of curvature near the beginning of the series. In the δ series the distance between successive lines increases continuously as the central maximum is approached, but in ϵ and ζ it passes through a maximum as in α.

* 'Astrophys. Jour.,' vol. 46, p. 85 (September, 1917).

BIRGE has found a hyperbolic relation between d_1 and m in the case of cyanogen, but it does not seem that this is applicable to the series under consideration, with the possible exception of ϵ and ζ. While it is possible to give approximate formulæ of the usual type for these series over a large part of their ranges, there seems little hope at present of finding any accurate formula which can be adapted to all of them. One can hardly resist the conclusion that there is some connection between the groups of three and the central maxima, but no numerical relation has yet been established.

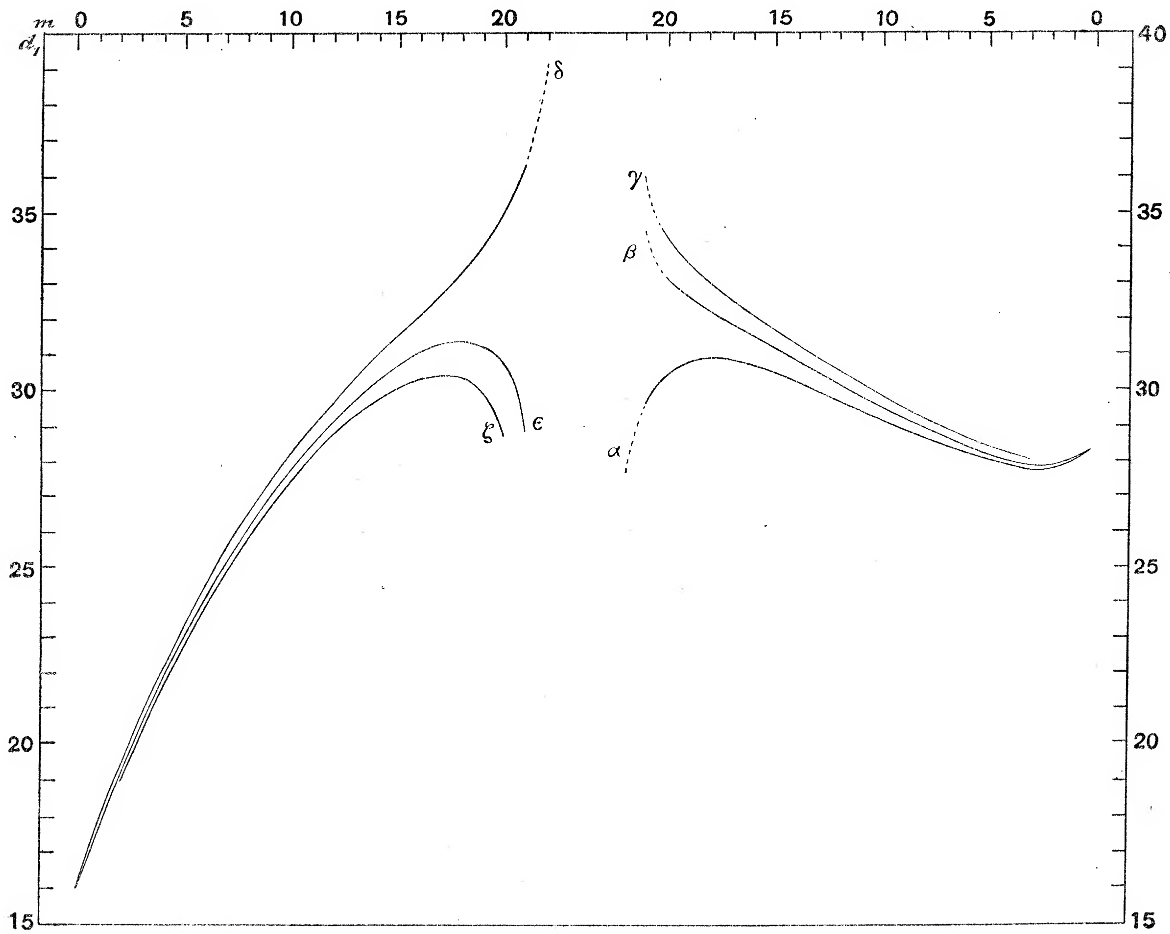


Fig. 2. Curves representing the varying distances between successive lines in the series α to γ. (The dotted portions of the curves are somewhat doubtful.)

It should be noted that in addition to the main series formed from the groups of three, there are other fragmentary series of fainter lines having intervals between successive lines of the same order of magnitude as those of the main series. These are indicated in the general table by α', α'', and δ'.

The Central Maxima.—The series which constitute the central and secondary maxima, so far as they have been identified, do not appear to present any unusual

features. In each case there are several superposed series, and some of the lines, which are probably unresolved composites, have to be assigned to two or more series. The probable series belonging to the secondary maximum have been designated a_1, a_2, a_3, and a_4; those on the red side of the chief maximum b_1 and b_2; and those on the more refrangible side of the chief maximum c_1, c_2, and c_3. There is some uncertainty as to the c series, as alternative arrangements of the lines appear to be consistent with series relationships.

The lines belonging to the various series are indicated in the general table, but a clearer idea of their character may be obtained from fig. 3, where the series are plotted to scale. The complete spectrum is first shown, with lines of lengths proportional to the intensities, and below these are drawn the separate series. It will be seen that a large proportion of the band lines fall into the nine series, and it is quite probable that all of them could be assigned to series if it were possible to employ still greater

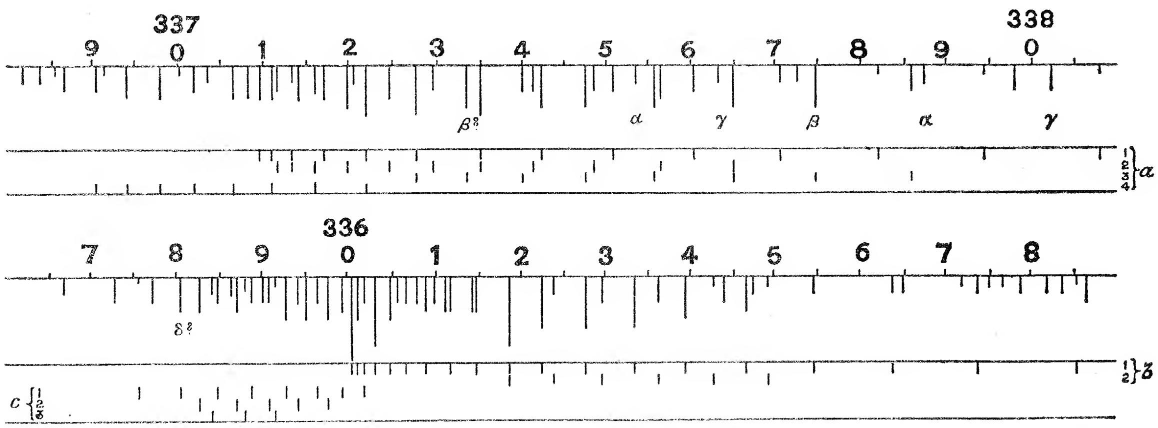


Fig. 3. Resolution of the central and secondary maxima into series.

resolving power. It will suffice to give numerical data for b_1 as a further indication of the characteristics of the series involved in the central maximum. These are shown in Table III.

The series is closely represented by the formula—

$$\nu = 29755{\cdot}176 - 0{\cdot}6935m + 0{\cdot}03327m^2 - 0{\cdot}008326m^3.$$

where m has values ranging from 3 to 21. The greatest deviation in wave-number is 0·41, corresponding to a difference of 0·045A between the observed and calculated values. The differences between the observed and calculated wave-numbers are shown in the last column of the table, and it will be seen that they are sufficiently systematic to indicate the imperfection of the formula. There would be no difficulty in calculating such formulæ for the other series, but it is not clear that they would serve any immediately useful purpose.

TABLE III.—Series b_1 of the Central Maximum.

λ, I.A.	ν, vac.	d_1.	d_2.	O – C.†
3368·53	29678·18			0·00*
		10·14		
67·38	88·32		1·2	+0·31
		8·99		
66·36	97·31		1·0	+0·41
		7·95		
65·46	29705·26		0·9	+0·35
		7·06		
64·66	12·32		0·8	+0·22
		6·28		
63·95	18·60		0·7	+0·11
		5·56		
63·32	24·16		0·6	0·00*
		4·95		
62·76	29·11		0·5	–0·03
		4·42		
62·26	33·53		0·7	+0·04
		3·72		
61·84	37·25		0·5	–0·01
		3·27		
61·47	40·52		0·5	+0·03
		2·75		
61·16	43·27		0·5	+0·03
		2·29		
60·90	45·56		0·3	0·00*
		1·95		
60·68	47·51		0·2	+0·02
		1·77		
60·48	49·28		0·3	+0·18
		1·50		
60·31	50·78		0·4	+0·37
		1·06		
60·19	51·84		0·3	+0·34
		0·80		
60·10	52·64		0·3	+0·24
		0·53		
60·04	53·17			0·00*

* Used in calculation of constants.
† O – C is expressed in wave-number.

Comparison with the Solar Spectrum.

Details of the comparison with the solar spectrum are included in the general catalogue of ammonia band lines given in Table V. To facilitate the comparison, the wave-lengths of the ammonia lines have been corrected to the scale of ROWLAND by the addition of 0·14A, as shown in the fifth column. The entries under "sun" are taken directly from ROWLAND'S table, and in the densest region of the central maximum, extending from 3363·5 to 3358·0, the solar lines have been tabulated in

full. A direct comparison of the two spectra in the neighbourhood of the central maximum is given in fig. 5, Plate 1, where the ammonia spectrum is reproduced as a negative in order to represent its appearance in absorption.

The comparison is complicated by the approximate coincidences of many of the ammonia lines with lines of metallic origin in the solar spectrum, or with unidentified lines which have intensities too great to allow of their being assigned to ammonia alone. As ROWLAND'S limit of resolution appears to be about 0·04A, ammonia lines may evidently be masked in this way by solar lines showing considerable differences in wave-length. Direct evidence of the presence of all the ammonia lines in the sun, such as would be afforded by identity of wave-lengths throughout, is therefore not to be expected.

There is also some uncertainty as to the completeness of ROWLAND'S list of wave-lengths, and as to the uniformity of his estimates of intensity. In this connection, a photograph of the solar spectrum in the HIGGS' collection of the Royal Astronomical Society has been to some extent utilised as a general check on ROWLAND in the region of the ammonia band. While the tabulated intensities on the whole were closely confirmed, there are several lines for which ROWLAND'S estimates appear to need revision. Attention is drawn to some of these in the column of remarks in Table V. As regards the wave-lengths, the relation between the international scale and the scale of ROWLAND is by no means simple. Comparison of the solar lines with the positions on the international scale given for the iron and nickel lines by BURNS shows that whilst the average difference in the region of the ammonia band is about 0·14A, there is no consistent agreement among the different lines. Deviations from the mean in a selected region frequently amount to nearly 0·01A, and there are occasional variations of 0·02A and upwards. These irregularities are not necessarily due wholly to errors of measurement, but may also be caused by differences in the effective level at which the various lines are produced in the solar atmosphere. It would seem, however, that if due regard be paid to intensities, coincidences within 0·02A may not be without significance.

Notwithstanding the difficulties affecting the comparison, there is abundant evidence that the ammonia band is present in the solar spectrum. The most convincing proof is perhaps afforded by the strongest part of the central maximum, extending from 3360·45 to 3360·08 (ROWLAND'S scale). As will be seen from fig. V., Plate 2, and from Table V., there is a complete correspondence of the solar and laboratory spectra as regards this group, except that the line 3360·45 may be slightly reinforced in the sun by a line of nickel.* This agreement is emphasised by the presence of a background of dark continuous spectrum which is sharply bounded in each of the two spectra by the outer two of the five lines involved. There is a similar dark ground covering the adjacent group 3360·82 to 3360·63, which is also clearly common to the two spectra.

* A nickel line in this position is given by ROWLAND, but not by EXNER and HASCHEK.

The coincidences in the case of the central maximum as a whole are scarcely less striking. The majority of the solar lines in this region in fact appear to be due to ammonia, as will be seen from the table, where the solar lines from 3363·4 to 3358·0 are tabulated in full in order to bring out this feature. In this small region there are 47 solar lines, at an average distance apart of 0·117A, and 37 ammonia band lines, at an average distance of 0·149A. Thirty-four of the ammonia lines are either represented directly by reasonably appropriate lines in ROWLAND'S table, or fall upon solar lines of recognised or probable metallic origins. The absence of one of the remaining three lines is satisfactorily accounted for by its low intensity. In the case of the outstanding lines 3361·61 and 3359·89, the solar line corresponding to the first appears to be masked by dark ground extending between the adjacent solar lines, while the second is probably included in the nebulous line 3359·936. The coincidences are clearly too numerous and too systematic to be considered accidental.* Confirmative evidence of their reality is afforded by the identity of narrow bright interspaces in the two spectra, especially those at 3361·0, 3360·9, 3360·5, 3360·0, 3359·7, and 3359·5, which will be clearly seen on reference to the photographs, these appear to be produced by patches of continuous background which are common to the two spectra. The discussion of the central maximum may thus be considered to establish the presence of ammonia in the sun beyond all doubt.

Analysis of the secondary maximum, occupying the region 3371 to 3378, leads to a similar conclusion, and there can be no doubt that the majority of the coincidences of lines of ammonia with faint solar lines in this part of the spectrum also have a real significance.

As regards the groups of three, forming the series α to ζ, there is also a close general agreement, and the few irregularities may well be caused by imperfect estimates of the wave-lengths and intensities in the two spectra, or by the approximate superposition of lines of other substances. If it were not for interference by metallic lines in the case of the sun, a good test would be provided by the series investigations. Supposing the coincidences to be genuine, the wave-lengths of the solar lines should show the series relations with the same order of accuracy as those of the ammonia lines themselves, and the intensities of the lines should be consistent with the series relationship. This test cannot be completely applied to any one of the six series, on account of near coincidences with metallic lines, but it may be worth while to take the chief lines of the δ series as an illustration. The facts with regard to these are collected in Table IV.

It will be observed that while three of the metallic lines (3341·967, 3320·783,

* In order to get a rough idea of the proportion of coincidences which might be merely accidental, the 37 ammonia wave-lengths in the region 3363·5 to 3358·0 were compared with the 47 solar lines from 3563·5 to 3558·0. The total number of approximate coincidences was 14, as compared with 34 in the true region, and of these, 5 were with lines assigned to metals. There was no systematic agreement of intensities in this case.

TABLE IV.—Evidence for δ Series in the Solar Spectrum.

Ammonia.				Sun.				
Intensity in arc.	λ (ROWLAND).	d_1.	d_2.	Origin.	Intensity.	λ.	d_1.	d_2.
4	3349·69				00	3349·695		
		3·93					3·934	
4	45·76		13		00	45·761		140
		3·80					3·794	
4	41·96		08	Ti	4	41·967		074
		3·72					3·720	
4	38·24		09		0	38·247		086
		3·63					3·634	
4	34·61		06		0	34·613		077
		3·57					3·557	
5	31·04		07		1N	31·056		034
		3·50					3·523	
5	27·54		08	Ni	2	27·533		119
		3·42					3·404	
5	24·12		07		0	24·129		058
		3·35					3·346	
4	20·77		09	Mn, Fe	2	20·783		077
		3·26					3·269	
3	17·51		07		0	17·514		089
		3·19					3·180	
3	14·32		10	Mn	0	14·334		084
		3·09					3·096	
3	11·23		10		0	11·238		097
		2·99					2·999	
3	08·24		10		0N	08·239		114
		2·89					2·885	
2	05·35				000	05·354		

3314·334) produce no appreciable disturbance of the first and second differences, some disturbance is caused by the unidentified line 3331·056, and by the nickel line 3327·533. If, however, the former be assumed to include a line shorter in wave-length by only 0·016A, and the latter to include a line of wave-length greater by 0·010A, the series connection would be shown as accurately by the solar lines as by those of ammonia.* The probable composite character of 3331·056 is in fact suggested by its nebulous appearance, and by its intensity being too great to allow of its being assigned wholly to ammonia. The agreement in the intensities is also satisfactory on the whole. The series investigation, so far as it goes, thus confirms the identification of some of the solar lines with band lines of ammonia. A general consideration of the intensities of the representatives of the α to ζ series in the solar spectrum appears to indicate a closer agreement with the arc than with the flame spectrum, the lines in the neighbourhood of the central maximum being relatively

* The second differences 077, 034, 119, 058 would then become 061, 076, 083, 068.

enfeebled in each case. This is in accordance with the fact that all the brighter lines composing the central and secondary maxima as seen in the arc, some of which do not occur in the flame, are represented in the solar spectrum.

The outcome of the comparison is to show that of the 260 band lines of ammonia in the region λ 3450 to λ 3286, there are about 140 which correspond with previously unidentified faint lines in the solar spectrum. About 100 of the remaining lines are obscured by lines for which metallic origins have been found, or fall upon lines which are too strong in the sun to be attributed entirely to ammonia, and the few which fail to appear in the sun are all of low intensity.

It may be that additional solar lines are identical with lines composing the bands of ammonia which appear in the visible spectrum, but there are at present no experimental data for effective comparison.

Description of Table V.

The first five columns of the table give details of the ammonia band lines, showing the series to which they have been assigned, the intensities in the flame and arc, and the wave-lengths on the international and ROWLAND scales. The following three columns show the wave-lengths, intensities, and origins of solar lines occupying about the same positions as the ammonia lines, as given by ROWLAND. Between λ 3363·5 and λ 3358·0 all the solar lines are tabulated, in order to show the large proportion due to ammonia in the region of the central maximum of the ammonia band. In the column of remarks, the following references have been adopted to avoid repetition.

(1) Solar line probably not wholly due to ammonia, as indicated by excessive intensity.

(2) Intensity of solar line probably over-estimated by ROWLAND, as inferred from a HIGGS' photograph.

(3) Very close ammonia lines, which are only vaguely resolved in the 3rd order of the 10-foot grating.

It should be noted that the resolving power in the case of the flame was less than that in the case of the arc spectrum.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons.

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
α, β		0	3450·36	3450·50	3450·469	5	Fe	
α, β		1	46·99	47·13	47·154	00N		
α, β		1	43·65	43·79	43·791	5*d* ?	Co	
α, β	0	2	40·36	40·50	40·505	0N		
γ		0	40·33	40·47				
α, β	1	3	37·06	37·20	37·190	3	Fe	
γ		0	36·99	37·13	37·116	000N		
α	1	2	33·78	33·92	33·905	0N		
β		2	33·74	33·88				
γ		1	33·65	33·79				
α	2	2	30·48	30·62				Probable faint solar line on edge of Zr 30·671.
β		2	30·41	30·55	30·545	00N		
γ		1	30·30	30·44	30·428	00		
α	2	2	27·15	27·29	27·263	3	Fe	
β		2	27·07	27·21	[27·220]	00		Solar line from HIGGS.
γ		1	26·93	27·07	27·046	0000		
α	3	2	23·81	23·95	23·972	0N		(2).
β		2	23·69	23·83	23·848	7	Ni	
γ		2	23·53	23·67	23·667	00N		
α	3	3	20·43	20·57	20·575	0		(2).
β		3	20·28	20·42	20·417	00		
γ	2	3	20·11	20·25	20·240	00		
α	4	3	17·04	17·18	17·198	00		
β		3	16·87	17·01	17·001	00		
γ	3	3	16·66	16·80	16·808	0		
α	4	4	13·64	13·78	13·782	0		
β		4	13·43	13·57	13·597	2	Ni	Not Ni in ammonia arc.
γ	3	3	13·18	13·32	13·275	5*d* ?	Fe	Ammonia may be included in solar lines.
α	3	4	10·22	10·36	10·386	1	Zr	
β	3	4	09·95	10·09	10·080	00		
γ	3	3	09·66	09·80	09·803	0		(2).
α'	00		09·20	09·34	09·346	2	Fe	
α	3	4	06·78	06·92	06·943	5*d* ?	Fe	
β	3	4	06·43	06·57	06·572	3	Fe	
γ	3	3	06·12	06·26	06·254	00		
α'	00		05·43	05·57				
α	4	4	03·31	03·45	03·478	2	Fe, Ti	
β	4	4	02·90	03·04	03·033	0		
γ	4	4	02·54	02·68	02·685	0		
α''	00		02·21	02·35	02·352	000		
α'	00		01·66	01·80	01·778	0000N		
α	5	4	3399·81	3399·95	3399·942	0N		
β	5	4	99·34	99·48	99·489	3	Fe	
γ	4	4	98·93	99·07	99·059	0		
α''	00		98·43	98·57	98·551	0000N		
α'	00		97·86	98·00				
α	6	4	96·30	96·44	96·437	0		
β	6	4	95·75	95·89	95·882	0		

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ ROWLAND.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
γ	4	4	3395·27	3395·41	3395·408	00N		
α''	00		94·64	94·78	94·746	3	Fe	
α'	00		93·99	94·13				
α	6	4	92·78	92·92	92·926	0	Ti	Not given as Ti by KILBY.
β	6	4	92·12	92·26	92·259	0		
γ	5	4	91·58	91·72	91·726	0		
α'	0	0	90·07	90·21				
α	6	5	89·23	89·37	89·387	00		
β	6	5	88·46	88·60	88·604	0N		
γ	5	5	87·84	87·98	87·988	5*d* ?	Ti, Zr.	
	0N		87·27	87·41				
	00	2	86·55	86·69	86·691	00N		
α'	0	1	86·13	86·27				
		1	85·87	86·01	86·005	0000N		
α	6	5	85·70	85·84	85·861	00	Fe ?	
	0	1	85·24	85·38	85·361	3	Co	
β	5	5	84·76	84·90	84·908	1		(1).
γ	4	5	84·07	84·21	84·225	00		
α, a_1	7	4	82·19	82·33	82·340	0		
β	5	3	81·04	81·18	81·202	0000		Corrected solar $\lambda = 81·170$.
a_1		1	80·78	80·92	80·889	1	Sr ?	
γ	4	3	80·22	80·36	80·397	3	Ti	
a_3		3	79·80	79·94	79·961	3	Cr	
a_1		1	79·43	79·57	79·577	000		
	0		79·25	79·39				
α	6	2	78·71	78·85	78·824	2	Fe	
a_3		3	78·58	78·72	78·723	00		
a_1		1	78·18	78·32	78·320	00		
a_3		5	77·48	77·62	77·622	3	Ti	
β	5	2	77·26	77·40	77·408	00		
a_1		2	77·04	77·18	77·202	0N	Co	
a_2, a_3		5*d* ?	76·48	76·62	76·630	2	Fe	
γ	4	2	76·29	76·43	76·414	0		(1).
a_1		3	76·01	76·15	76·164	00		
a_2		4	75·62	75·76	75·768	000		Arc includes faint Cu } (3).
a_3		5	75·57	75·71	75·698	1	Ni	,, ,, ,, Ni }
α	6	2	75·33	75·47	75·478	0N		
a_1		3	75·08	75·22	75·231	00		
a_2		3	74·84	74·98	74·981	000		
a_3	0	5	74·75	74·89	74·872	1	Zr	
a_1		5	74·23	74·37	74·358	4	Ni	Arc includes faint Ni.
a_2		3	74·14	74·28	74·271	000		
a_3		3	74·00	74·14	74·119	2		(1).
a_1, a_2		6	73·50	73·64	73·642	0		
a_3, β ?	5	5	73·34	73·48	73·452	0		Solar line probably double.
		0	73·12	73·26				
a_2		3	72·95	73·09	73·105	0N		(1).

Table V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
a_1, a_3	2	6*d* ?	3372·77	3372·91	3372·901	5	Ti, Pd	
a_2		4	72·46	72·60	72·609	00N	Fe	
a_1, a_4	6	6*d* ?	72·19	72·33	72·314	0		Also series α ?, γ ?
		2	72·06	72·20	72·225	1	Fe	
a_2		5	71·99	72·13	72·124	4	Ni, —	Arc includes faint Ni.
a_1	1	4	71·71	71·85	71·852	00		
a_2, a_4		3	71·61	71·75	71·745	000		
		4	71·39	71·53	71·535	00		Difficult group in arc, which includes a faint metallic line.
a_1, a_2	1	?	71·34	71·48				
a_2		3	71·15	71·29	71·296	00		
a_1, a_4		4	71·10	71·24	71·246	00		
a_1	6 {	4	70·97	71·10	71·110	0		
		4	70·81	70·95	70·933	4	Fe	
a_4	1	4	70·62	70·76	70·770	1N*d* ?	Zr, Mn	
		0	70·44	70·58	70·584	2	Ti	
	2 {	2	70·31	70·45	70·468	2	Co	
a_4		3	70·18	70·32	70·330	0N		(2).
		1	70·02	70·16	70·173	00		(1).
a_4	2	4	69·78	69·92	69·932	0		
a_4	4	3	69·38	69·52	69·506	0N		
		1	69·17	69·31				
a_4	4	3	69·03	69·17	69·190	0		
	2	3	68·65	68·79	68·793	00		
b_1		1	68·53	68·67	68·680	00		(1).
	0 {	2	68·36	68·50	68·496	000		
		2	68·18	68·32	68·319	1	Mn	
	2	2*d* ?	67·87	68·01	68·029	2	Ti, Ni, Fe	
		1	67·67	67·81	67·812	0		(1).
		1	67·49	67·63				
b_1		2	67·38	67·52	67·527	0000		
		1	67·18	67·32	67·297	1	Fe ?	
		2	66·47	66·61	66·594	000		
b_1		2	66·36	66·50	66·494	000		
		0	65·96	66·10				
b_1	00	2	65·46	65·60	65·581	0		(1).
b_2	1	1	64·93	65·07	65·081	0000		
		2	64·73	64·87	64·832	00		Corrected solar λ = 64·870.
b_1	00	4	64·66	64·80	[64·786]	00		Solar line added from Higgs.
	1	3	64·38	64·52	64·535	0N*d* ?		
b_2		1	64·26	64·40	64·408	1	Co	
b_1	1	5*d* ?	63·95	64·09	64·055	0		Solar line wide enough to include ammonia.
b_2	0	3	63·61	63·75	63·750	1	Ni	
b_1	1	6	63·32	63·46	63·442*	0*d* ?	Co	*
					63·298	0000N		

* From 3363·4 to 3358·0 the solar lines are tabulated in full.

Table V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
b_2	00	3	3362·97	3363·11	3363·107	0		
b_1	2	6	62·76	62·90	62·936	4N*d* ?	Co	
					62·782	1		
					62·727	0000		
b_2		2	62·38	62·52	62·528	0		
b_1	3	6	62·26	62·40	62·402	2*d* ?		(1).
					62·275	1		
					62·087	2	Ti	
b_1, b_2	6	8	61·84	61·98	61·988	0		
					61·906	1		
					61·704	3N*d* ?	Co	
b_1	1	4	61·47	61·61				Solar line merged in dark ground.
		4	61·42	61·56	61·568	0N		
					61·421	2		
b_1	4	4	61·16	61·30	61·327	8	Ti	
		4	61·10	61·24	61·241	1		(2).
		3	60·98	61 12	61·141	0		
b_1		4	60·90	61·04	61·055	1	Ti	
		3	60·80	60·94	60·988	0		Corrected solar λ = 60·942.
b_1	3	3	60·68	60·82	60·828	0		Dark ground, both in sun and ammonia.
		3	60·58	60·72	60·741	0		
b_1		5	60·48	60·62	60·631	0		
					60·485	1	Cr	
b_1	10	8	60·31	60·45	60·444	2	Ni	Ni not given by Exner and Haschek.
b_1, c_1		3	60·19	60·33	60·345	0		Dark ground, both in sun and ammonia.
b_1		5	60·10	60·24	60·258	0		
b_1		10*d* ?	60·04	60·18	60·181	2		
c_1		4	59·94	60·08	60·066	0		
c_2 ?		5	59·75	59·89	59·936	1N		Solar line wide enough to include ammonia.
					59·823	2		
c_1		3	59·63	59·77	59·769	1		(1).
	4	5	59·50	59·64	59·636	2	Fe ?	
c_2		3	59·41	59·55	59·542	1		(2).
c_1		5	59·28	59·42	59·420	1	Co	
c_3		1	59·15	59·29				
c_2		3	59·08	59·22	59·248	3N	Ni	Not Ni in ammonia arc.
		3	59·02	59·16	59·144	00		
c_1	3	3	58·89	59·03	59·035	2N		(1).
c_3		1	58·80	58·94	58·929	00		(2).
c_2		4	58·70	58·84	58·832	0		
		2	58·65	58·79	58·771	00		(2).
c_1	4	3	58·48	58·62	58·649	4	Ti, Cr	
c_3		2	58·42	58·56	58·542	00		(2).
c_2		4	58·28	58·42	58·416	3	Ti	
					58·276	0000		

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity. Flame.	Intensity. Arc.	Wave-length. I.A.	Wave-length. Rowland.	λ Rowland.	Intensity.	Origin.	
c_1, δ?	5	4	3358·04	3358·18	3358·182	1N		
					58·076*	0000		*
	5	3	57·72	57·86	57·874	0		
c_1		0	57·56	57·70	57·703	0		(1).
	5	3	57·28	57·42	57·412	2	Zr	
	4	2	56·66	56·80	56·821	2	Fe	
	2	1	55·18	55·32	55·363	4	Fe	
	1		53·91	54·05	54·057	000N		
δ	6	2	53·63	53·77	53·768	00N	Zr	
	0	1	53·10	53·24	53·262	2		(1).
	1		51·77	51·91				
ε	3	1	50·85	50·99	50·985	000		
		0	49·85	49·99				
δ	10	4	49·55	49·69	49·695	00		
δ'	0	0	48·68	48·82	48·820	000		
	0	0	47·94	48·08	48·072	3	Fe	
ε	4	2	47·62	47·76	47·760	00N		
ζ	3	0	46·42	46·56	46·557	0		(1).
		2	46·28	46·42	46·414	00		
δ	8	4	45·62	45·76	45·761	00		
δ'	0	1	44·86	45·00	45·015	000		
ε	5	2	44·17	44·31	44·315	00		
ζ	4	1	43·21	43·35	43·366	0		(1).
	1	1	43·01	43·15	43·156	00		
	0	1	42·33	42·47	42·442	3	Fe	
δ	8	4	41·82	41·96	41·967	4	Ti	
δ'	00		41·15	41·29	41·300	0000N		
ε	6	2	40·68	40·82	40·823	00N		
ζ	6	3	39·86	40·00	40·011	1		(1).
	0	?	39·30	39·44	39·438	000N		Possibly obscured in arc by "ghost."
	0	0	38·80	38·94	38·944	0000		
δ	8	4	38·10	38·24	38·247	0		
		1	37·67	37·81	37·803	3	Fe	
ε	6	4	37·19	37·33	37·319	1N	Co	
		1	36·75	36·89				Possibly obscured in sun by Mg 36·820 (8N).
ζ	6	2	36·49	36·63	36·635	00N		
δ	7	4	34·47	34·61	34·613	0		
ε	7	4	33·72	33·86	33·854	0		
		2	33·40	33·54	33·526	2	Co	
ζ	7	3	33·11	33·25	33·250	0		
		1	33·05	33·19				
δ	7	5	30·90	31·04	31·056	1N		
		1	30·59	30·73	30·745	000	Sn ?	
ε	7	5	30·27	30·41	30·438	1		
ζ	6	4	29·75	29·89	29·902	00		
		1	28·19	28·33	28·341	00	Co	

* From 3363·4 to 3358·0 the solar lines are tabulated in full.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
δ	6	5	3327·40	3327·54	3327·533	2	Ni	
ε	5	4	26·87	27·01	26·998	3	Ti	
ζ	5	4	26·41	26·55	26·553	0		
δ	5	5	23·98	24·12	24·129	0		
ε	5	4	23·53	23·67	23·669	0		
ζ	5	4	23·12	23·26	23·256	00		
δ	4	4	20·63	20·77	20·783	2	Mn, Fe	
ε	4	3 ?	20·25	20·39	20·391	7	Ni	Obscured in arc by Ni.
ζ	4	3	19·89	20·03	20·032	0		
δ	3	3	17·37	17·51	17·514	0		
ε	3	3	17·04	17·18	17·174	00		
ζ	3	3	16·73	16·87	16·871	00		
δ	3	3	14·18	14·32	14·334	0	Mn	
ε	3	3	13·90	14·04	14·042	00N		
ζ	3	3	13·63	13·77	13·774	1		(1).
δ	3	3	11·09	11·23	11·238	0		
ε	3	3	10·85	10·99	10·996	0		
ζ	3	3	10·62	10·76	10·777	1N		(1).
δ	3	3	08·10	08·24	08·239	0N		
ε		3 ?	07·90	08·04	08·035	00N		Obscured in arc by Cu.
ζ	2	2	07·70	07·84	07·845	4	Fe	
δ	2	2	05·21	05·35	05·354	000		
ε		2	05·05	05·19	05·194	000		
ζ	2	2	04·87	05·01	05·001	00	Mn	
δ	2	2	02·42	02·56				Obscured in sun by Na 02·510 (6).
ε		2	02·30	02·44	02·443	0000N		
ζ	1	1	02·15	02·29	02·289	0000N		
δ	2	2	3299·76	3299·90	3299·905	0		(1).
ε		2	99·67	99·81	99·804	0		(1).
ζ		1	99·54	99·68	99·652	0N*d* ?	Mn	
δ	2	1	97·23	97·37	97·381	0		(1).
ε		1	97·16	97·30	97·301	0	Co	
ζ		0	97·05	97·19	97·194	0N		(1).
δ	1	1	94·82	94·96	94·949	00N		Just resolvable in 4th order plate.
ε		1	94·79	94·93				
ζ		0	94·70	94·84	94·849	000		
δ, ε	1	1	92·58	92·72	92·728	4	Fe	
ζ		0	92·51	92·65	92·636	0		(1).
δ, ε	0	1	90·50	90·64	90·642	0N		(1).
ζ		0	90·45	90·59	90·602	00		
δ, ε	0	1	88·57	88·71	88·705	2	Ti	
δ, ε		0	86·84	86·98	86·980	0N		(1).

Description of Plate.

Fig. I. is enlarged from a photograph of the spectrum of the flame of ammonia fed with oxygen; taken with a small quartz spectrograph. The bright band on the left is due to water vapour.

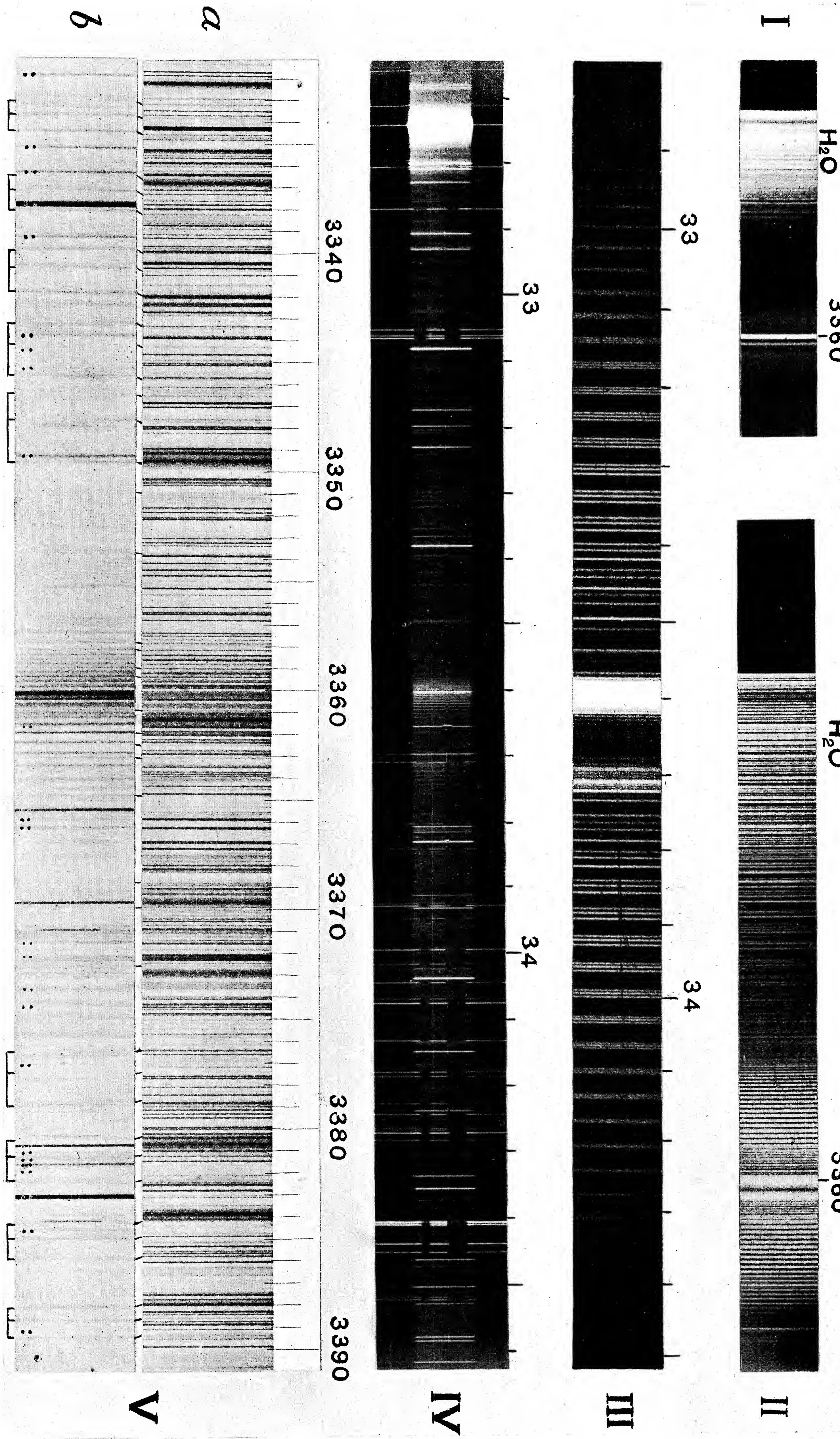
Fig. II. is from a photograph taken with a quartz spectrograph of moderate dispersion, the source being a flame of imperfectly dried cyanogen burning in an atmosphere of oxygen. The bright band on the left is due to water vapour.

Fig. III. shows the band of the ammonia flame as photographed with the large quartz spectrograph.

Fig. IV. is from a photograph taken in the 3rd order of a 10-foot concave grating. The short lines at the edges are those of the iron comparisons. The middle spectrum is that of the copper arc in ammonia.

Fig. V. (*a*) is the solar spectrum, from a photograph by HIGGS; (*b*) is the copper arc in ammonia, as fig. IV. It is shown as a negative to facilitate comparison with the solar absorption lines. Metallic lines are marked by double dots, except in the case of iron comparison lines, which are short lines along the middle of the spectrum. The scale is that of ROWLAND. (There is a slight difference of scale of the two enlargements, but several lines common to the two spectra are indicated.)

THE AMMONIA BAND, λ 3360



THE AMMONIA BAND, λ 3360